Endohedal fullerenes C_{60} and C_{82} with silver

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Abstract

The models of endofullerenes C_{60} and C_{82} with silver atom or diatomic silver are calculated with *ab initio* SCF Hartree-Fock methods including the full geometry optimization. Ag@C_{60} is a bound system with positive binding energy while Ag$_2$@C_{60} is not because strong geometrical strain. Silver atom is located at some distance from the cage center in the lower-energy model, and the structure reduces the symmetry. The endo-structures with the C_{82} cage can exist with both mono- and diatomic silver. Electronic charge transfer in all structures occurs from the carbon cage to silver.

Key words: Endohedral fullerenes, silver, clusters, SCF calculations
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1 Introduction

Endohedral fullerenes with metal atoms and clusters are of interest as species in which interaction of metal and carbon atoms can be either of the Van der Waals nature (if size of the fullerene cage is enough large) or through the metal-carbon chemical bonding due to overlap of carbon and metal atomic orbitals [1,2]. The stable C_{60} molecule with closed π-electronic system is not very active reagent for metal atoms, the higher fullerenes C_{70}, C_{82}, C_{84}, etc. are more reactive, and possibility to keep metal atoms and clusters evidently is more for them. C_{82} is considered as one of 'magic' higher endofullerenes [3]. The endohedral fullerenes with rare earth elements were produced and theoretically evaluated in many works [2,4,5], however, silver was not considered to date for our knowledge. It was reported in [6] on interaction products of silver atoms with C_{60} molecules, but no information is available on possibility of endo-position of silver. Meanwhile, silver atoms and small clusters can be stabilized

in solutions and solid matrices [7], and they are of essential interest from many point of view. Silver clusters and nanoparticles were produced also in carbon nanotubes [8,9] those can be treated as close analogs of fullerenes possessing another topology. It should be noticed that elements with easy capability to form endohedral fullerenes have a low ionization energy evidencing that the ionization process is an important step in formation of $M_n@C_m$, and electron acceptor ability of fullerene is also a key factor. Silver has the ionization energy 7.6 eV that is very close to the known value of C_{60} [10]. This can be a reason of different properties of endofullerenes with silver, if they can exist, as compared with endofullerenes with active metals. Electronic structure of these species should be more complicated due to strong hybridization of atom orbitals (AO) of silver and carbon [11].

In the present work, we consider a series of models built from fullerene molecules C_{60}, C_{82}, silver atoms and diatomic silver. They were calculated with *ab initio* SCF Hartree-Fock methods with full geometry optimization, and possibility of existence and some properties of the models are evaluated.

2   Calculation methods

Model structures under study are displayed in Fig. 1: mono-atomic endo-structures and the fullerene cages with diatomic Ag_2. They are pictured as optimized, initial positions of one Ag atom was the centre, and for $Ag_2@C_{60}$ we placed two atoms along z-axis (C_5 axis for C_{60} and C_3 for C_{82}). A principal possibility to embed diatomics may be not excluded knowing the typical interatomic distances of Ag_2, about 2.5 Å[12], and the size of C_{60} cage, 7.1 Å. We estimate stability through the binding energies defined with respect to a decay into free atoms or Ag_2 and empty C_{60} or C_{82} those were calculated at the same level of theory.

The task on minimum energy geometries was done for ground states: doublets for mono-atomic endofullerenes and singlets for the models with Ag_2. For empty C_{60} and C_{82} singlet states are most probable for stable species. The calculation method used was the self-consistent (SCF) Hartree-Fock (HF) (unrestricted for doublet states) within the molecular orbital - linear combination of atomic orbitals (MOLCAO) approach and density functional theory (DFT) with B3LYP functional. The basis functions were constructed with the 19-electronic effective core potential (ECP) for Ag and the all-electronic set of STO-3G quality for carbon atoms. Initial coordinates of carbon atoms for C_{60} were generated within the I_h symmetry from one unique atom position (C_5 axis was directed as z), and for C_{82} they were taken from [13]. The calculations were done with a NWChem 4.1-4.5 software [14]. The basis sets were used within this package library with no modifications. Effective charges for
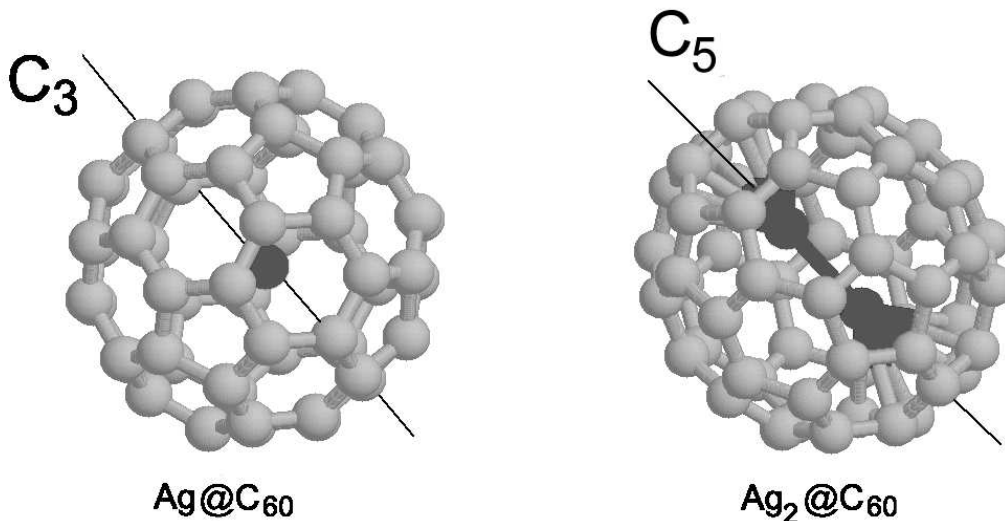
Fig. 1. Models with C_{60}

atoms were calculated from Mulliken occupancies of the optimized structures.

A final geometry was searched by the full optimization allowing any distortion from the initial I_h or C_{3v} symmetry for the structures with C_{60} and C_{82}, respectively, and metal atoms were also allowed to change positions arbitrary, thus the final structures of minimum total energy were obtained.

It should be noticed that the present choice of calculation method for the endofullerenes with silver seems not to be very simplified, though SCF HF may not be considered as highly adequate for many systems. We need analyse asymmetrical clusters having 82 carbon atoms and 2 silver atoms, and we use ECP only for silver that is commonly accepted for this metal. Carbon atoms are treated with rather short basis set, however, the known results for empty C_{60} are reproduced quite sufficiently, and the calculation with 6-31G basis is given for comparison. A full symmetry breaking strongly enlarges the task. An account of electronic corelations would be fruitful, however, within the framework of this paper we analyse only geometry of ground states, and they will be considered in future for calculation of more properties. We present also the test calculations wit DFT in which electronic correlation is taken into account for the selected models, and the results are in quakitative consistence with the SCF HF method.
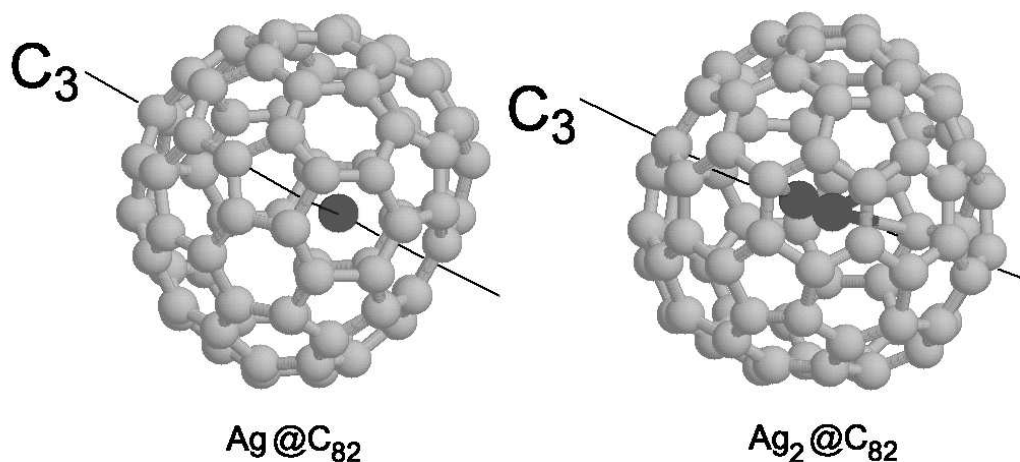
Fig. 2. Models with C_{82}

3 Results and Discussion

3.1 Ag@C_{60}

The structure Ag@C_{60} is quite stable according to the value of binding energy. The value of 10.15 eV means that the hypothesis on Ag@C_{60} has the theoretical ground. Very recently [15] Cu@C_{60} was shown to be produced by collision of evaporated C_{60} molecules with copper plasma. As far as properties of copper and silver are rather close we may suggest possibility of similar production of Ag-containing endofullerene.

The calculated Ag@C_{60} appears to be noticeably deformed from the perfect initial geometry of C_{60}. The deformation looks as the axial extension of the whole cage, the minimum C-C distance grows on 0.2 Å, and the maximum one does on 0.8 Å. The structure losses initial symmetry by the geometry optimization procedure, and the final one possesses the C_3 symmetry, silver atom is placed on the axis crossing the centres of opposite hexagons (Fig. 1). The shift of endohedral silver atom is about 0.28 Å. It should be remarked that a displacement of atoms and ions inside the C_{60} cages (as well inside C_{70}, C_{80}, C_{82}, etc.) is familiar phenomenon of endofullerene science [16,17], and often this displacement appears to be even more. The shift of the endohedral silver atom occurs approximately (but not exactly) along the C_3 axis, however, the calculation keeping the C_3 symmetry does not provide energy lower than the value calculated without symmetry (C_1). Table 2 presents the numerical data for Ag@C_{60} calculated keeping different symmetry, and the data with additional calculation with DFT confirm the conclusions of HF calculations. The lowest energy structures are not symmetrical. These geometrical features

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Table 1
Selected interatomic distances in the optimized models with C_{60} and C_{82}, Å, and effective charges at silver atoms (in units of e). For C_{60} the results are given for two basis sets: STO-3G/6-31G

Model	Min C-C	Max C-C	M-M	BE, eV	Ag1	Ag2
C_{60}	1.38/1.37	1.46/1.45				
$Ag@C_{60}$	1.40	1.54		10.15	-0.1	
$Ag_2@C_{60}$	1.36	1.51	2.37	-24.23	-1.34	-1.34
C_{82}	1.34	1.49				
$Ag@C_{82}$	1.36	1.55		16.5	-0.08	
$Ag_2@C_{82}$	1.34	1.50	2.57	3.3	-0.16	-0.33

were not reported for endofullerenes with the C_{60} cage for another metals. Likely, complicacy of silver atoms electronic structure can be a reason of this phenomenon.

The calculated values of effective charges in the optimized clusters is -0.1 that means the interaction of silver atom is not very strong, and the charge transfer exists from the C_{60} cage to silver atom. s-type orbitals from silver atoms contribute dominantly to highest occupied MO (HOMO) like to the chemical bond formation in the case of alkali metals, but the charge transfer direction shows that silver in this case does not behave as typical s-metal. The reason of this fact can be the lower energy level of s-orbitals for silver than for the more active metals. In the other words, chemical intuitive fact of the lower electron-donor ability of silver is consistent with these result on charge transfer.

3.2 $Ag@C_{82}$

The structure $Ag@C_{82}$ was not touched for calculations to date. From several isomers existing for C_{82} we took the example with C_{3v} symmetry, and the arbitrary geometry distortion was allowed during calculation. The final endo-structure appeared to be of the lower symmetry, C_s only. Silver atom distorts the cage rather strongly (Fig. 2, Table 1), but an interaction of Ag with carbon atoms in the optimized stable structure is weak since the effective charge calculated to be only -0.08 (less than in $Ag@C_{60}$). The value of binding energy amounts about 16.5 eV. In contrast with $Ag@C_{60}$, in the case of silver atom within C_{82} an essential admixing of p-type AOs of Ag occurs that can be a reason of the strong geometry distortion.

Table 2
Comparison of total electronic energies (Hartrees) calculated with the two methods (SCF HF and DFT) for symmetric (Ag atom in the centre) and asymmetric Ag@C_{60} models and coresponding displacement of the central atom, D, Å

Symmetry	Energy (HF)	D (HF)	Energy (DFT)	D (DFT)
I_h	-2389.4572	0	-2404.0437	0
C_1	-2389.4782	0.28	-2404.0438	0.17
C_3	-2388.5994	0.01	-2404.0435	0.14

3.3 $Ag_2@C_{60}$

The calculation of binding energy for the models with diatomic silver cluster within C_{60} (Fig. 1) does not argue on its stability. The interatomic distance Ag-Ag in the optimized structure is 2.37Å(approximately on 0.2 Å less than in bare diatomic Ag_2 [12]), i.e. Ag_2 is very strained that provides its instability within the cage, which cannot be extended keeping C-C bonds unbroken. C_{60} cage is also subjected to distortion (Table 1). Effective charges at metal atom are higher than in the above structure with one silver atom. An analysis of energies of the frontier orbitals in the models with diatomic clusters within C_{60} indicates that formation of $Ag_2@C_{60}$ rises both HOMO and LUMO levels. HOMO is contributed by d-type AOs of silver together with p-AOs of carbon. Thus, this model is instable mainly due to geometrical reasons, and we may expect that larger cages can keep the silver clusters with more probability.

3.4 $Ag_2@C_{82}$

In the calculations of silver diatomic clusters within C_{82} we took also one isomer of C_{82} with C_{3v} symmetry and placed initially the Ag-Ag bond along the C_3 axis. The optimization method with no symmetry restriction could relocate silver atoms to any other direction if structures of the lower energy appear. Fig. 2 illustrates the final structure in which the Ag_2 cluster is shifted ≈ 0.1 Å from the axis. However, the deformation of C_{82} cage is less than in the above case of Ag@C_{82}. It is worth to remember that one silver atom even within C_{60} aspires not to be in the centre. The interatomic distance Ag-Ag is not much lower than in the bare silver diatomics (Table 1), and the value of binding energy of this structure is about 3.3 eV showing thus that it can exist. HOMO of this structure is contributed mainly by $s-$AOs of silver with admixture of $p-$AOs of silver. Thus, $Ag_2@C_{82}$ model can be proposed also as a candidate for real structures.

4 Conclusions

The present work with calculations of $Ag_n@C_{60}$ and $Ag_n@C_{82}$ ($n = 1, 2$) models is the first attempt, for our best knowledge, of the theoretical analysis of silver endofullerenes. There existed a priori feasibility to embed Ag atom and Ag_2 molecule into both C_{60} and C_{82} from geometrical opinion. The calculations performed at the *ab initio* SCF HF level showed that these expectations are not too far from reality. The structures $Ag@C_{60}$, $Ag@C_{82}$ and $Ag_2@C_{82}$ can exist, but the fullerene cages are essentially distorted from initial perfect symmetry, and positions of silver atoms are off-centre. Silver does not provides electron-donor property of active metal in all endofullerenes consideed.

Acknowledgements

References

[1] *Endofullerenes. A New Family of Carbon Clusters* T.Akasaka and S.Nagase (Eds) (Kluwer Academic Publishers: Dordrecht, 2002).

[2] L. Forro and L. Mihaly, Rep. Prog. Phys. **64**, (2003) 649.

[3] B.L. Zhang, C.Z. Wang, K.M. Ho, C.H. Xu, and C.T. Chan, J. Chem. Phys. **98**, (1993) 3095.

[4] Sh. Nagase, K. Kobayashi, and T. Akasaka, Bull. Chem. Soc. Jpn. **69**, (1996) 2131.

[5] J. Cioslowski and E.D. Fleischmann, J. Chem. Phys. **94**, (1991) 3730.

[6] J.A. Howard, M. Tomietto, and D.A. Wilkinson, J. Am. Chem. Soc., **113**, (1991) 7870.

[7] A. Henglein, J. Phys. Chem. **97**, (1993) 5457.

[8] J. Sloan, D.M. Wright, H.-G. Woo, S. Bailey, G. Bown, A.P.E. York, K.. Coleman, J.L. Huchison, and M.L.H. Geen, Chem. Commun (1999) 699.

[9] P. Corio, A.P. Santos, P.S. Santos, M.L.A. Temperini, V.W. Brar, M.. Pimenta, and M.S. Dreselhaus, Chem. Phys. Lett. **383**, (2004) 475.

[10] A.F. Hebard, Annu. Rev. Mater. Sci. **23**, (1993) 159.

[11] I. Laslo, Fullerene Sci. and Technol. **1**, (1993) 11.

[12] M.D. Morse, Chem. Rev. **86**, (1986) 1049.

[13] http://www.cochem2.tutkie.tut.ac.jp/Fuller/fsl/fsl.html

[14] R. Harrison, J.A. Nichols, T.P. Straatsma, M. Dupuis et al. *NWChem, A Computational Chemistry Package for Parallel Computers, Version 4.5.* (2004, Pacific Northwest National Laboratory, Richland, Washington 99352-0999, USA).

[15] H. Huang, M. Ata, and Y. Yoshimoto, Chem. Commun. (2004) 1206.

[16] D.M. Poirier, M. Knupfer, and J.H. Weaver, W. Andreoni, K. Laasonen, M. Parrinello, D.S. Bethune, K. Kikuchi, and Y. Achiba, Phys. Rev. **B49** (1994) 17403.

[17] Y. Lian, Shangfeng Yang, and Shine Yang, J. Phys. Chem. **B106**, (2002) 3112.